*Review Paper:*

# Acid rain and its effect on aquatic ecosystem: A critical review on plants

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***Abstract***

*Acid rain is one of the serious environmental problems in recent days. It creates a major impact on terrestrial as well as aquatic ecosystems. The main purpose of the review is to emphasize the impact of acid rain on the aquatic ecosystem. The main contributing factors to acid rain are the release of nitrogen dioxide, sulphur dioxide and ozone into the atmosphere. The important effect of acid rain is eutrophication which means over-enrichment of lakes and pond. Acid rain creates a impact on lake and stream by increasing the concentration of nitrogen and sulphur in the water which leads to the loss of buffering capacity and leads to the death of aquatic organisms.*

*Acid rain influences the metabolic activity of aquatic animals. At very low pH levels, adult fishes tend to die. Acid rain affects the aquatic plants by impacting an effect on leaf micromorphology, leaf organelles, photosynthesis, enzyme activities and causes damage to plant leaves. Acid rain has wet and dry deposition forms. Legislations should be made available to control the effect of acid rain to save the biodiversity.*

**Keywords:** Acid Rain, Aquatic plants, Ecosystem, Sulphur dioxide.

## Introduction

The Earth has given humans an environment abundant with natural resources, comprising of the elements Prithvi (earth), Jala (water), Vayu (air), Akasha (space) and Agni (fire). This nature in the hands of humans, is under the most pressure in various aspects to fulfill the unbounded needs of these rival scavengers. Human beings, regardless of considering these natural resources as common to all living beings, take them and get covered and determined in the hands of few, resulting in enormous depletion and unequal distribution leading to many problems. Currently, the nature is closely linked to both the exploitation and limited restoration of natural resources. To be more explicit, there are many types of pollution and their corresponding effects. In today's fast-paced society, we often neglect basic needs such as eating, sleeping and working, but never overlook the essential act of breathing.

Furthermore, it is crucial to preserve and label our existence. Beneath an apparent problem of pollution lies a grave situation exacerbated by its devastating consequences. Therefore, it expects a crucial and necessary debate regarding the significant and dangerous consequences of acid rain. Acid rain poses a detrimental and dangerous environment for the viability of both living and non-living elements. Furthermore, it has a wide-ranging impact on both terrestrial and aquatic ecosystems, thereby disrupting their biodiversity.

Acid rain was initially observed in European countries during the mid-19th century. Ducros was the first scientist to observe acid rain in the year 1845. In 1852, Robert Angus Smith became the first person to establish a connection between acid rain and atmospheric pollution in Manchester, England. In 1872, Smith coined the term "acid rain" [10] and in the late 1960s, scientists initiated an investigation and observation of the phenomenon in order to uncover the underlying events that would maintain the mysterious nature of the subject among the scientific community, thereby stimulating debates and discussions aimed at elucidating the notions and achieving widespread acceptance.

Acid rain, also known as acid deposition, refers to any type of precipitation that contains acidic substances such as sulphuric acid or nitric acid, that falls from the atmosphere in either wet or dry forms. Additionally, it encompasses other type of precipitation that exhibits high acidity, characterized by higher concentrations of hydrogen ions[24]. This encompasses various forms of precipitation such as rain, snow, fog, hail, or even dust particles that possess acidic properties. The majority of water, including water suitable for consumption, typically has a pH level that falls between the neutral range of 6.5 to 8.5. However, acid rain has a lower pH level, averaging around 4-5, which is below the neutral range[50]. It has a crucial impact on causing environmental harm and cross-border contamination, which includes lasting consequences. Acid rain is characterized by the presence of very acidic water droplets which result from significant quantities of sulphur dioxide and nitrogen dioxide[55].

## Sources of Acidic Pollutants

Acid rain occurs when precipitation takes on an acidic nature due to the presence of carbon dioxide in the atmosphere. The main cause of this phenomenon is the combustion of fossil fuels such as coal, oil and gas in domestic and industrial activities, as well as other contributing elements that generate sulphur dioxide and nitrogen oxides. These pollutants can elevate the acidity levels of rain and other forms of precipitation. The sources of oxides of nitrogen, sulfur and other harmful substances can be either naturally

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occurring such as volcanoes, oceans, biological decay and forest fires, or they can result from combustion processes in industries that generate the required output sources through chemical and physical reactions.

The increasing demand for electricity and the rise in the number of motor vehicles in recent decades has increased acidifying pollutants dramatically since the 1950s. Emissions of such pollutants are heavily concentrated in the northern hemisphere, especially in Europe and North America[4]. As a result, precipitation is generally acidic in these countries. From the late 1970s and 1980s, Scandinavian countries such as Denmark, Sweden and Norway from northern Europe noticed the effects and impacts of acid deposition on trees and freshwaters. Much of the pollution causing this damage in their country was identified as being transported from other polluting countries. Hence, acid rain becomes an international concern.

## Causes of Acid Rain

There are multiple factors contributing to the occurrence of acid rain. The main contributing factors to acid rain are the release of nitrogen dioxide, sulphur dioxide and ozone gases into the atmosphere[21]. Sulphur dioxide and nitrogen oxides are released into the atmosphere by volcanic eruptions, earthquakes, natural fires, lightning and some microbiological processes. The primary hazardous volcanic gases in volcanic eruptions are sulphur dioxide, carbon dioxide and hydrogen fluoride. On a local scale, the presence of sulphur dioxide gas from a volcano can result in the formation of acid rain and air pollution in areas located downwind. These gasses are emitted from lava flows and the explosive eruption of a volcano.

Nevertheless, the primary source of sulphur dioxide emissions is human activity, specifically the combustion of fuels in industrial and power plant settings. Additionally, motor vehicles are responsible for half of the nitrogen oxide emissions, as they release gasses that contribute to this pollution[43]. Forest fires, vegetation degradation and biological processes also emit substantial amounts of gases, resulting in the formation of acid rain. Dimethyl sulfide is a significant biological source of sulphur-containing compounds in the environment.

The formation of nitrogen dioxide in the atmosphere is mostly due to anaerobic biological interactions in the soil/water and photochemical destructions. Lightning activity generates nitric oxide which combines with water to create nitric acid, a crucial component of acid rain[21]. In addition, extensive cattle farming generates ammonia through the decomposition of organic matter, leading to formation of nitric acid in the atmosphere but, it is of lesser extent. These pollutants, which can travel vast distances from their source, react with the environment and produce sulphuric acid and nitric acid[4]. These acids dissolve in water droplets within the clouds and precipitate onto the Earth's surface as acid rain, which can also manifest as snow or fog. Acid rain is a consequence of chemical reactions occurring in the environment. Acid rain, characterized by its low pH and high aluminum content, causes numerous chronic stressors in aquatic species.

## Effects of Acid Rain

The ecological effects of acid rain are most clearly seen in aquatic or water ecosystems such as streams, lakes and marshes. Acid rain falling on forests, fields, buildings and roads will move to streams, lakes and marshes. Acid rain also falls directly on aquatic habitats and causes damage to them. Mostly, lakes and streams have pH between 6 and 8 excluding some lakes which are naturally acidic. Acid rain primarily affects watersheds whose soils have a less ability to neutralize acidic compounds, called buffering capacity. Lakes and streams become acidic when the water surrounding the soil cannot react with the acid rain to neutralize it. In areas where buffering capacity is low, acid rain releases aluminum from soils into lakes and streams which is highly toxic to many species of aquatic organisms.

**1. Effect on lake and stream:** Lakes are one of the essential aquatic ecosystems supporting water life. Acid rain is one of the results of various anthropogenic activities which harm the lakes to a greater extent. They have buffering capacity to balance their fluctuating pH levels, to support aquatic life. However, their long time deposition causes the concentration of nitrogen and sulphur compounds to be increased in the water, resulting in the loss of their buffering capacity and slowly, its water becomes acidic, resulting in the death of aquatic life[11]. The countries like Norway have been suffering from acidification of lakes, which has also reduced their freshwater availability. Most of the European countries, the US and Canada, are also suffering from these problems.

Many lakes and streams examined by National Surface Water Survey (NSWS) on 2000 suffer from chronic acidity, a condition in which water has a constant low pH level[23]. The survey investigated the effects of acidic deposition in approximate 1,180 lakes and 4670 streams more believed to be sensitive to acidification. Acid rain caused acidity in 75 percent of the acidic lakes and about 50 percent of the acidic streams[28]. Streams flowing over soil with low buffering capacity are also susceptible to damage from acid rain as lakes[27]. Approximately 580 of the streams in the Mid-Atlantic coastal plain are acidic primarily due to acidic deposition.

**2. Eutrophication of lake:** Eutrophication can be defined as the over-enrichment of minerals and nutrients in water bodies such as lakes and ponds. This excessive growth of algae in the lake is called an algal bloom, which covers lake surfaces with a green blanket. Eutrophication depletes the dissolved oxygen and increases the biochemical oxygen demand of water. It also prevents the entry of sunlight and gaseous exchange from the lake water, resulting in the loss of underwater plant and animal species. Excess accumulation of nitrogen, phosphate and organic compounds is the major cause responsible for the eutrophication of lakes.

However, acid rain is another essential reason behind eutrophication in lakes. As acid rain reaches the ground, it solubilizes several available nutrients in the soil, which ultimately reaches the nearby water bodies. This continuous flow of such water leads to nutrient enrichment and causes eutrophication in lakes[35]. Dal lake is one of the famous lakes in Srinagar, Jammu Kashmir, India and is slowly dying due to eutrophication. Thus, the freshwater availability for the cities, as well as the aquatic life forms, have decreased in the lake[31].

**3. Effect on fish and other aquatic organisms:** Acid rain causes several effects that harm or kill individual fish, reduce fish population, eliminate fish species from a waterbody and decrease biodiversity[48]. As acid rain flows through soils in a watershed, aluminum is released from soils into the lakes and streams located in that watershed. So, as pH in a lake or stream decreases, aluminum levels increase. Both low pH and increased aluminum levels are directly toxic to fish. It also causes chronic stress that may not kill individual fish but leads to lower body weight and smaller size and makes fish less able to compete for food and habitat. Some types of plants and animals can tolerate acidic waters. Generally, the youngest species are more sensitive to environmental conditions than adults. At pH 5, most fish eggs cannot hatch. At lower pH levels, some adult fish die. Some acid lakes have no fish[21].

Aquatic ecosystem has a wide range of biotic components like autotrophs and heterotrophs. Acid rain lowers the acidity of the water bodies as water has a lower acid buffering capacity than soil. Thus, acid rain changes the acidity of the lake. Acid rain also releases aluminium from soil to the lakes and streams, which is highly toxic to aquatic life such as algae, mosses, phytoplankton and consumers. Phytoplankton is an essential source of food for filter-feeding crustaceans and rotifers. Many of them are very sensitive to low pH levels and thus disappear from water bodies after acid rain[40].

**4. Effect on ecosystem:** Biological organisms and the environment in which they live, from an ecosystem. The plants and animals living within an ecosystem are highly interdependent. For example, frogs may tolerate relatively high levels of acidity, but if they eat insects like the mayfly, will get affected and also part of their food supply may disappear. The connections between the many fish, plants and other organisms living in an aquatic ecosystem are inter dependent. If there are changes in pH or aluminum levels, they will affect the aquatic biodiversity. Thus, as lakes and streams become more acidic, the numbers and types of fish and other aquatic plants and animals that live in these waters, decrease[53]. Thereby, acid rain affects the terrestrial ecosystem by harming their environment.

Acid rain has varied effects on different ecosystems and environments including both terrestrial and aquatic habitats. Some effects of acid rain are listed as follow:

- Acid rain causes the oceans to lose their biodiversity and productivity. The lowering of the pH of marine waters harms phytoplankton, a food source for different organisms and animals, which can modify the food chain and can lead to the extinction of different marine species.
- Inland waters are also acidifying at a very rapid rate which is particularly worrying as although only 1% of the planet's water is fresh, 40% of fish live in it. This acidification increases the concentration of metal ions mainly aluminum ions which could lead to the death of many fish, amphibians and aquatic plants in acidified lakes. In addition, heavy metals are transported to underground waters, which become unsuitable for consumption[45].
- In forests, the low pH level of the soil and the concentration of metals such as aluminum prevent vegetation from adequately absorbing the water and nutrients. This damages roots, slows growth and makes plants weaker and more vulnerable to diseases and pests[29].
- Acid rain also affects artistic, historical and cultural heritage. In addition to corroding metallic elements of buildings and infrastructures, it deteriorates the external appearance of monuments. The most significant damage occurs to calcareous constructions such as marble, which gradually dissolve because of acids and water[58].

Acidification causes death of aquatic plants and has a significant impact on amphibians[16]. Many amphibians are susceptible to acidification because at different pH levels, different species can live.

**Table 1**
**pH of various waters in comparison with acid rain**

| S.N. | Types of water | pH Level | Acid Rain pH |
|---|---|---|---|
| 1 | Tap water | ~7.5 | 5 to 5.5 |
| 2 | Distilled reverse osmosis water | 5 to 7 | |
| 3 | Common bottled water | 6.5 to 7.5 | |
| 4 | Bottled water labelled as alkaline | 8 to 9 | |
| 5 | Ocean water | About 8 | |

## Effect of Acid Rain in Plants

Plants necessitate an ideal pH level in order to sustain their existence. Acid rain changes the pH of the water, which in turn impacts plant growth. Acid rain depletes the minerals and nutrients in the submerged soil, which are crucial for optimal plant growth[53]. Additionally, it has wider impact on the process of photosynthesis. Juvenile plants are the most susceptible ones [49,50]. The available oxygen content for the plant is significantly impacted. Plants utilize the oxygen present in the water, also absorb the acid, ultimately leading to their demise. Duckweed and Elodea are capable of thriving in pH levels of 5. But, acid rain droplets extract nutrients from plant leaves. It facilitates the dissolution of essential elements such as magnesium and calcium, which provide plants with the ability to resist illnesses and insects. Hence, acidophilic plants exhibit rapid mortality in reaction to acid precipitation[57].

Aquatic plants, also known as hydrophytes, are evolved to thrive in habitats with waterlogged conditions. These encompass a variety of habitats, ranging from aquatic environments such as deep water to terrestrial places like bogs and marshes. Based on physiological and morphological adaptations, these plants were classified into two types. The first category is helophytes, these are plants that have their roots beneath but have stems that emerge above the water, where they develop leaves and reproductive structures e.g. lilly, lotus, water caltrop, Chinese water Chesnut, water spinach etc. The second category, hydrophytes, these are plants that are specifically adapted to live immersed in water e.g. water hyacinth. The hydrophytic plants can be categorized into different species based on their characteristics.

The roots firmly attached to the substrate below, able to float freely, having leaves and/or reproductive parts submerged underwater, or having leaves and/or reproductive parts above the water surface[19,24]. The occurrence of aquatic plants is largely dependent on the depth and speed of water flow and water quality. If the quality of water depletes due to acid rain, the life of plants will be disturbed. Acid rain has an essential effect on plants, as it ceases vital activities and growth by regulating plant-associated soil microorganisms. Acid rain helps in inducing soil acidification and nutrient deficiency. It causes enormous environmental problems and has adverse effects on plants globally. Acid rain deposition on parts of the plants, such as leaf, flower, shoot, stem, etc. causes the early death of the plant.

## Effect on plant leaf

**1. Effect on leaf micromorphology:** Acid rain negatively impacts leaf micromorphology by weakening the protective waxy layer on the surface and damaging the outer layer of cells, epidermis. This, in turn, has detrimental effects on the process of plant photosynthesis. Acid rain causes damage to the outer layer of plants and alters the structure of guard cells in leaves, as well as causing certain alterations in the inner tissue[2,7,42]. In water hyacinth, both the epidermal and mesophyll cells collapse, resulting in the hypertrophy of parenchymatous spongy tissues[25].

**2. Effects on leaf organelles:** Acid rain causes disturbances to the cell organelles and mesophyll tissue found in leaves, resulting in harm to specific organelles such chloroplasts and mitochondria. According to Chen et al[8], acid rain damages cell walls and cell membranes by creating mitochondrial ridges. Furthermore, acid rain can result in the distortion of chloroplasts and disrupt the grana, leading to the removal of crests[20,26,32]. Observation of plasmolyzed guard cells and rupturing of cuticle in necrotic areas can be seen in water hyacinth, as described by Bjerregaard et al[5].

**Effect on photosynthesis in leaf:** Acid rain significantly affects the process of photosynthesis. Photosynthesis is a vital and essential physiological process of plants[13]. To produce oxygen, it is essential to ensure an acid-free atmosphere, as this is highly important for human survival. Exposure of carbon dioxide to acid or acid rain can have detrimental effects on physiological functions including the erosion of the hydrophobic coating on leaf surfaces that aids in water regulation, damage to chloroplasts and the extraction of acid-induced base cations in mesophyll cells[14]. The affects can lead to change in certain plant taxonomy, life cycle stages and pH levels[33,54]. Non-woody plants are more vulnerable to the harmful effects of acid rain than woody plants, as demonstrated by studies conducted by Sant'Anna-Santos et al[42].

Dong et al[14] observed that acid rain can actually increase the rate of photosynthesis in leaves of woody plants when they absorb nitrates from the acid rain, leading to a beneficial outcome. The chlorophyll ratio in water hyacinth increased when the intensity of the rising irradiance was adjusted. Cosby et al[9] found that acid rain does not harm mature leaves, but it reduces the ability of both stomata and mesophyll in younger leaves, both in the short and long term.

**4. Effects on enzyme activities and metabolism:** Acid rain causes a series of changes in plant membrane permeability. Enzymatic activities lead to synthesis of free radical antioxidants and plant metabolism[34,39,53,57]. Acid rain damages the natural enzymatic and non-enzymatic pathways. Acid rain helps in creating more number of reactive oxygen species inside the cell. Superoxide dismutase enzymes is involved in the first step of defense against super oxide radicals. Catalase, the second step of defense, involves the destruction of $H_2O_2$, which is produced in the cell when acid rain falls on the plant[22].

Nitrate reductase plays a vital role in nitrogen metabolism and nitrogen uptake by plants and is related to the uptake and use of N by plants. Increased acid rain intensity causes decreased nitrate reductase levels in plants[38,46]. In water hyacinth when exposed to acidic conditions, reduced nutrient uptake, brown leaves and withered plants were observed in initial stages[13].

**5. Apparent damage to plant leaf:** Acidified ocean causes changes in physical, chemical and biological changes in leaves[44]. The leaves of aquatic plants will expose symptoms such as yellow-brown and black-brown necrotic spots at the margin and in between the veins, excessive greenness, curl, wilting and abscission on or after acid rain[17,18,30]. Acid rain at pH 5 damages woody and non-woody plants and causes necrotic spots on the leaf surface[55]. The older leaves show small brown spots at pH 3.0[45,52]. Some conclusions were made in response to acid rain: (1) wilting of standard epidermal cells and structural damage of stomatal guard cells at pH 4.5, (2) interveinal and marginal necrotic dots, (3) cracking of epicuticular wax, (4) turgidity loss, (5) modification of epidermal cell, (6) hypertrophy of parenchymatous cells, (7) collapse of epidermal and mesophyll cells at pH 3.0, (8) necrotic spots, (9) cuticle changes and (10) areas of total tissue destruction at pH 2.5[2,3,41,56]. The same effects were observed in water hyacinth such as decreased photosynthesis and chlorophyll uptake in long term and short term, poor mobility of nutrients, withered leaves with brown discoloration[13].

## Effect on plant growth

**1. Effect on length of aquatic plant:** The severity of acid rain often has a substantial impact on plant height or stem height. Acidic conditions frequently lead to a decrease in the size of underwater plants due to the inhibition of plant growth[1].

**2. Effect on weight of aquatic plant:** Low pH and high aluminum levels lead to a toxic effect especially reduction in weight of the aquatic plants. Further acidity causes stress that reduces the weight of the plant below the water surface[37].

**3. Effect on plant reproduction:** Aquatic plants become highly sensitive on response to acid rain. Due to higher level of sensitivity, most of the aquatic plants die before reaching reproductive stage[36].

## Wet and dry deposition of acid precipitation

Acid rain is a detrimental phenomenon caused by the presence of certain pollutants in the atmosphere, resulting in rain that becomes acidic. It falls under the category of acid deposition, which can manifest in various forms. One form is wet deposition wherein rain, sleet, snow, or fog become more acidic than usual. Another form is dry deposition which involves the transformation of gases and dust particles into acidic substances. The wind can transport these forms of acid deposition over significant distances[47].

As acid deposition occurs, it affects not only the environment but also affects various structures and organisms. Buildings, cars and trees are all susceptible to the corrosive effects of acid deposition. Additionally, lakes can be negatively affected by acidic precipitation, leading to increased acidity levels. In the case of dry deposition, people can inhale acid particles and gases, which can result in health issues for specific individuals.

Dry deposition occurs explicitly when minuscule acidic particles and gases descend upon the Earth's surface. Notably, gases like Sulphur dioxide and nitrogen oxides undergo chemical reactions upon contact with water, transforming into acids. When referring to acid precipitation, it encompasses any form of aqueous precipitation that has a higher acidity level than carbon dioxide ($CO_2$). It encompasses both wet and dry forms of acid deposition[6]. Dry deposition primarily transpires near the emission source as the acid gases and compounds settle onto the Earth's surface. On the other hand, wet deposition can occur thousands of kilometers away from the original emission source, as wind currents can carry it for extensive distances.

## Effect of Acid Rain in Aquatic Animals

Acid rain affects the metabolic activities of many animals especially digging and spawining behaviour in brown trout (*Salmo trutta)* and the result was compared with those in Hime (*Landlocked sockeye*) and Salmon (*Oncorhynchus nerka*). The spawning brown trout was found to be extremely sensitive towards the acidity of water, especially pH below 5 and the nest-digging behavior was inhibited. The female trout and salmon showed no digging below pH 5.0 and 6.0 respectively. When the pH of ambient water returned to nearly neutral conditions, these two species behaved differently.

The digging in hime and salmon reappeared in 4 of 6 fishes tested[24], whereas in brown trout, the digging behavior reappeared in all tested fishes. The spawning behavior is significantly reduced in an acidic environment and that is the reason for the reduction of the salmonid population in the early stage of acidification.

The regular activities of animals also get affected by acid rain. When the effect of low pH (4.5) condition was examined on endocrine and immune function in carp (*Cyprinus carpio*), the hormone plasma cortisol levels showed a drastic significant increase (about 100 ng/ml) as early as 3hr after the initiation of low pH exposure and remained high for two days. Cortisol levels decreased to 8.14 ng/ml after one week but were still significantly higher than those of control (pH 7.0). The immune response also showed some variations due to acid rain. The plasma levels of antibodies also decreased[19].

At lower pH, some adult fishes die and the most important aspect is that at pH 5, most fish eggs cannot hatch[57]. If so in extreme cases if the fishes survive the animals on consumption of these fishes get adversely affected. Due to acidification of ocean, the prey capturing ability and early life of octopus are drastically affected[12].

## Conclusion

Acid rain is the result of toxic emissions of nitrogen dioxide and sulfur dioxides from various sources. When these emissions react with rainwater, the pH of the resulting rainwater becomes highly acidic, ranging from 5 to 5.6. This acidity is harmful to human life, damaging to infrastructure and unsuitable for consumption. Acid rain significantly affects both terrestrial and aquatic ecosystems, compromising their sustainability and development. This issue, along with other contributing factors, has garnered attention and concern from the public, prompting collective efforts to enhance future protection measures. However, when considering the aquatic ecosystem, the impacts and harm caused by it are once again diverse and varied.

The impact on the metabolism of aquatic plants and the detrimental decrease in their ability to tolerate and adapt to the unpredictable environment are also significant factors. Acid rain has interconnected impacts that disrupt the entire cycle in which it overlaps or depends on many functions, affecting their life processes. It also significantly impacts the markets and the related sectors that rely on or establish their core units inside these aquatic environments. Therefore, it is important to address the concerns that emphasize the need for a major initiative to rectify and to mitigate the errors that contribute to the occurrence of acid rain.

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